UDC 666.11.01:539.213.2:239.217

DEPENDENCE OF THE COHESION FACTOR OF ALKALI-SILICATE GLASS STRUCTURE ON SILICA MODULUS

E. F. Medvedev[1] and A. I. Khristoforov[1]

Translated from Steklo i Keramika, No. 8, pp. 8 – 10, August, 2003.

A correlation between the structure cohesion factor and the silica modulus is identified based on analysis of calculated data. Nomograms and a prediction method are proposed to determine the specified parameters. The advisability of using the silica modulus as a structure-determining criterion in designing glass for hydrogen microcontainers is demonstrated.

As the sphere of glass application expands, new requirements on its properties arise, which had not been an object of study before, such as, for instance, hydrogen permeability. The absence of suitable methods for developing compositions markedly complicates chemical engineering research, considering that at least 83 out of the 109 elements known [1] are used to obtain different varieties of glass, and the number of possible combinations is infinite. The main principle of material science implies that a composition determines a structure, and the structure determines properties; therefore, the problem of predicting properties based on prescribed structural parameters is topical for reducing the factor of indefiniteness at the stage of developing compositions.

The main components of most industrial glasses are SiO_2 and Na_2O. The ratio of their molar contents C is called the silica modulus n_{Si}, which is calculated from the formula [2, 3]

$$n_{Si} = \frac{C_{SiO_2}}{C_{Na_2O}}.$$

In vitrification of liquid (melt), its lattice formed by the least mobile particles (in silicate glasses tetrahedrons [SiO_4]) freezes, and glass become solid. To characterize the lattice formed, N. N. Ermolenko [4] proposed the structure cohesion factor Y:

$$Y = \frac{\sum_j x_j C_j z - \sum_k x_k C_k}{\sum_j x_j C_j},$$

where x is the number of actions in the oxide; z is the valence (coordination number) of the respective metal; k are oxides containing cations with number of bonds equal to unity (alkali cations, halides); j are oxides containing cations with number of bonds higher than unity.

The study in [4] describes crystallochemical patterns and their cohesion factor values: at $Y = 4$, a continuous three-dimensional lattice is formed due to bridge oxygen atoms; at $Y = 3$, a two-dimensional laminar lattice; at $Y = 2$ a unidimensional lattice is formed by polymeric chains; and at $Y < 2$, single isolated fragments or short two-link chains are formed, in which case formation of glass is impossible.

The purpose of the present study was to prove the dependence of the cohesion factor on the silica modulus and the possibility of using it to predict the glass structure.

We investigated the following glass groups: silica, borosilicate, aluminosilicate, and aluminoborosilicate: altogether 99 compositions (RF patents Nos. 2033978, 2036171, and 2036856, U.S. patent No. 4257799) [1, 5 – 10]. In all compositions SiO_2 was the main glass-forming agent and Na_2O was the modifier. Table 1 lists the values of the silica modulus and the cohesion factor.

Figure 1 shows the curves $Y = f(n_{Si})$ for each group of glasses. It can be seen that the cohesion factor grows exponentially with increasing modulus. The curve $Y = f(n_{Si})$ for the integrated group of compositions is shown in Fig. 2, the approximating function being an exponent of the form

$$Y = -1.63 \exp\left(-\frac{n_{Si}}{t}\right) + 3.45,$$

where t is a constant coefficient equal to 2.35.

Setting the modulus values as multiples of the coefficient t, according to the equation found, one can calculate the cohesion factor values and then construct a respective curve (Fig. 3).

[1] Russian Federal Nuclear Center – All-Russia Research Institute of Experimental Physics, Sarov, Russia; Vladimir State University, Vladimir, Russia.

TABLE 1

n_{Si}	Y	n_{Si}	Y	n_{Si}	Y	n_{Si}	Y
Silicate glasses							
2.71	2.87	5.23	3.13	5.39	3.29	106.53	3.98
5.17	3.10	5.25	3.29	17.92	3.45	–	–
Borosilicate glasses							
1.53	2.44	3.22	3.07	2.88	3.19	15.14	3.39
1.79	2.52	3.08	3.13	2.56	3.18	5.59	3.38
1.82	2.64	2.99	3.13	3.67	3.23	7.13	3.53
9.48	3.12	3.07	3.14	3.55	3.25	3.26	3.54
2.88	3.04	3.34	3.08	2.91	3.21	29.15	3.56
2.84	2.99	3.06	3.17	58.78	3.42	12.47	3.46
2.85	3.00	3.35	3.18	3.39	3.27	67.74	3.60
2.56	2.99	3.24	3.19	12.07	3.32	94.63	3.90
5.82	3.18	3.35	3.21	23.61	3.40	–	–
Aluminosilicate glasses							
4.08	3.02	4.65	3.27	4.94	3.21	5.23	3.28
4.22	3.16	4.69	3.25	4.94	3.23	5.38	3.27
4.31	3.28	4.82	3.22	4.94	3.26	5.62	3.30
4.34	3.30	4.85	3.34	5.16	3.28	6.52	3.33
4.58	3.18	4.88	3.27	5.17	3.26	11.22	3.43
Aluminoborosilicate glasses							
1.52	2.44	5.31	3.33	11.62	3.42	16.45	3.59
2.80	2.95	6.35	3.28	11.71	3.53	17.27	3.59
3.00	2.98	6.43	3.32	12.28	3.36	17.44	3.57
3.09	3.08	7.39	3.46	13.09	3.37	18.60	3.50
3.55	3.10	7.52	3.27	13.77	3.42	19.53	3.59
4.00	3.12	7.63	3.25	14.47	3.39	20.98	3.59
4.30	3.12	7.89	3.36	15.78	3.49	22.14	3.60
4.97	3.26	9.77	3.40	16.10	3.42	22.17	3.61
5.00	3.24	11.32	3.40	16.40	3.36	–	–

Calculation of the Cohesion Factor Based on the Model Equation

Silicate modulus	Cohesion factor
$0.25t$	2.21
$0.5t$	2.49
$0.75t$	2.71
t	2.88
$1.25t$	3.00
$1.5t$	3.12
$2t$	3.26
$3t$	3.40
$4.25t$	3.46
$12.5t$	3.48
$15t$	3.48
$20t$	3.48

It follows from analysis of the calculation data and the shape of the curve $Y = f(n_{Si})$ that $Y_0 = 3.48$ is the upper limiting value for the considered group of alkali-silicate glasses. According to the data in [3], this value corresponds to the formation of a two-dimensional laminar structure with three-dimensional lattice elements. The highest value of the cohesion factor value ($Y = 4$) is possible only in quartz glass and glasses with similar compositions (high-silica), when a three-dimensional structural lattice is formed; however, quartz glass does not belong to the system considered.

The most alkali-rich phases in the $Na_2O - SiO_2$ system are sodium pyrosilicate $3Na_2O \cdot 2SiO_2$ and sodium orthosilicate $2Na_2O \cdot SiO_2$ [1, 2]. Orthosilicate as the main phase is unfavorable for glass formation: its structure is represented by single isolated fragments $[(SiO_{4/2})^{4-}\,3Na^+]$ that do not have bridge oxygen ions needed for the construction of a coherent lattice. Bridge oxygen ions are formed starting with pyrosilicate with $n_{Si} = 0.67$, when two-unit chains consisting of fragments $[(SiO_{4/2})^{4-}\,3Na^+]^-$ are formed. Glass formation is presumably facilitated by phases formed by groups $[(SiO_{4/2})^{4-}\,2Na^+]^{2-}$ and $[(SiO_{4/2})^{4-}\,Na^+]^{3-}$, which contain two

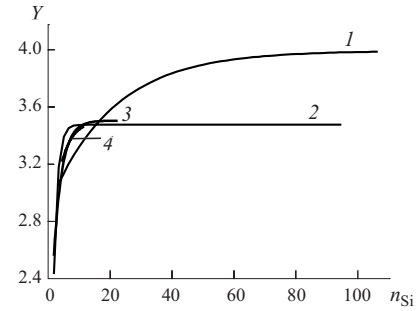

Fig. 1. Variations of logarithms of the structure cohesion factor and silica modulus of glasses based on the $Na_2O - SiO_2$ system split by groups of glasses: *1*) silicate; *2*) borosilicate; *3*) aluminoborosilcate; *4*) aluminosilicate.

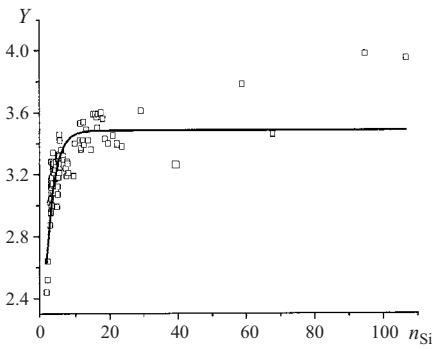

Fig. 2. Variation of logarithms of the structure cohesion factor and silica modulus of glasses based on the $Na_2O - SiO_2$ system in integrated group of glasses: □) all compositions; $Y = A \exp(-n/t) + Y_0$ (A is constant), $Y_0 = 3.48$, $A = -1.63$, $t = 2.35$.

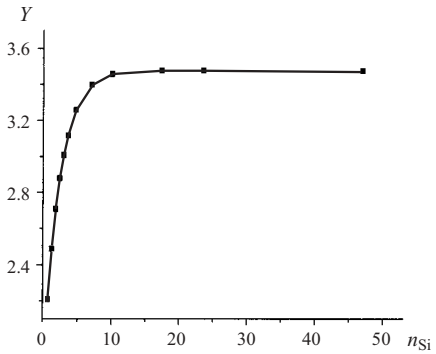

Fig. 3. Variations of the structure cohesion factor of glasses calculated based on the regression equation.

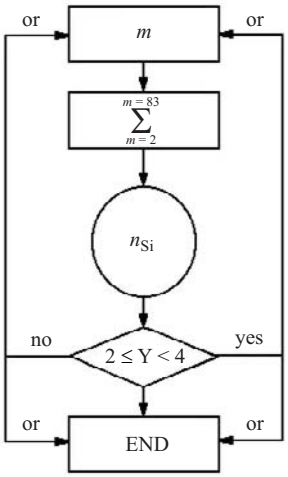

Fig. 4. A search block scheme for prediction of silicate modulus, structure cohesion factor, and hydrogen permeability of glasses based on the $Na_2O - SiO_2$ system: block "*m*") a set of components for compositions; block $\sum_{m=2}^{m=83}$) a glass-forming composition; block "n_{Si}") verification of silica modulus value; block "2 ≤ Y < 4") verification of the glass-formation condition based on factor *Y*; block "END") end of search.

to three bridge oxygen ions that participate in the formation of two- and three-dimensional lattices: the first group is typical of sodium monosilicate and the second is typical of sodium disilicate. Consequently, glass formation in an alkali-silicate system based on $Na_2O - SiO_2$ is possible on the condition that $2 \le Y < 4$. In the integrated groups of glasses $2.44 \le Y \le 3.48$, with $1.52 \le n_{Si} \le 106.63$ (Table 1). It is necessary to take into account the data from [11, 12], according to which quartz glass and high-silica glasses of similar compositions with $n_{Si} \to \infty$ are the most gas-permeable.

Taking into account the above and considering that $z_{Si} = 4$, $x_{Si} = 1$, and $x_{Na} = 2$, Ermolenko's formula was reduced to the following form:

$$Y = \frac{\left(4C_{SiO_2} + \sum_p x_p C_p z_p\right) - 2\dfrac{C_{SiO_2}}{n_{Si}} + \sum_q x_q C_q}{C_{SiO_2} + \sum_p x_p C_p},$$

where *p* are all oxides containing cations with quantity of bonds greater than unity, without taking into account SiO_2; *q* are oxides containing cations with number of bonds equal to unity without considering Na_2O.

After the transformation, the Ermolenko formula explicitly corroborates the dependence of the structure cohesion factor on the silica modulus.

It is easy to determine one of the criteria from the curve shown in Fig. 3. if the other one is known. Accordingly, the following method is proposed for analysis of compositions in developing hydrogen microcontainers. Based on a preset value of silicate modulus, the ratio of the main components is found for microcontainer glass developed in the $Na_2O - SiO_2$ system. Next, the structure cohesion factor is found from the reference curve $Y = f(n_{Si})$ (Fig. 3). Using both criteria and taking into account the data from [11, 12], the hydrogen permeability can be predicted. In the case of a positive answer, the glass composition, if necessary, can be further complicated by introducing new ingredients, and for each new ingredient the procedure of verifying the cohesion factor and gas permeability is repeated again. A search block scheme for this method is shown in Fig. 4.

In order to optimize the final composition, at least two projected compositions have to be compared. It should be admitted that the method proposed is rather cumbersome in the case of a multicomponent glass although it is advantages to a chemist; for instance, one can improve the chemical resistance or other parameters. However, the use of the method proposed makes it possible to substantially minimize the factor of indefiniteness in determining the qualitative composition of glass and avoid unwarranted expenses of materials resources. Furthermore, this method can presumably be used as well in other cases, where silica modulus and the structure cohesion factor are significant.

Consequently, the silica modulus should not be considered only as a trivial mathematical expression of a concentration ratio of the main glass-forming component SiO_2 to the main modifier Na_2O. This modulus determines the cohesion factor, i.e., the type of structural lattice of glass within the $Na_2O - SiO_2$ system. The modulus ought to be used as the main criterion in developing glass compositions, in particular those intended for making hydrogen microcontainers.

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